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(54) LITHIUM-CONTAINING TRANSITION METAL MULTIPLE OXIDE AND MANUFACTURING METHOD THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a positive electrode active material for a lithium secondary cell having a wide usable voltage range, the excellent durability against charge/ discharge cycle, high capacity and safety.

SOLUTION: The lithium-containing transition metal multiple oxide, in which the average number of valency of nickel-manganese-metal element M in a lithium-containing nickel-manganese-metal element M multiple oxide for a lithium secondary cell is 2.700-2.970, is used as the positive electrode active material for the lithium secondary cell.

The lithium-containing nickel-manganese-metal element M multiple oxide for a lithium secondary cell is formed by firing a nickel-manganese-metal element M multiple compound and a lithium compound and is expressed by a general formula, LiNixMn1-x-yMyO2 (where, (x) and (y) are respectively $0.30 \leq x \leq 0.65$, $0 \leq y \leq 0.2$ and M represent a metal element selected from Fe, Co, Cr, Al, Ti, Ga, In and Sn).

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CLAIMS

[Claim(s)]

[Claim 1]General formula $\text{LiNi}_x\text{Mn}_{1-x-y}\text{M}_y\text{O}_2$ (however, it is $0.30 \leq x \leq 0.65$ and $0 \leq y \leq 0.20$.) A metallic element as which M is chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. It is expressed, A lithium containing transition metal multiple oxide for lithium secondary battery positive active material, wherein average valences of an element which consists of nickel, manganese, and the metallic element M are 2.700-2.970.

[Claim 2]The lithium containing transition metal multiple oxide according to claim 1, wherein it is R-3-m rhombohedron structure and specific surface area is below $2\text{-m}^2/\text{g}$.

[Claim 3]The lithium containing transition metal multiple oxide according to claim 1 or 2, wherein a grating constant of an a-axis is 2.895-2.925Å and a grating constant of c axis is 14.28-14.38Å.

[Claim 4]A lithium containing transition metal multiple oxide given in any 1 paragraph of claims 1 thru/or 3, wherein exothermic starting temperature is not less than 255 **.

[Claim 5]A lithium containing transition metal multiple oxide given in any 1 paragraph of claims 1 thru/or 4, wherein granular material press density is more than 2.9 g/cm^3 .

[Claim 6]It is the method of manufacturing a lithium containing transition metal multiple oxide of a statement in any 1 paragraph of claims 1 thru/or 5, A manufacturing method of a lithium containing transition metal multiple oxide mixing a nickel manganese metallic element M coprecipitation conjugated compound and a lithium compound, and calcinating this mixture at 500-1000 ** in an inert atmosphere.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the improved lithium containing transition metal multiple oxide which is used as positive active material of a lithium secondary battery.

[0002]

[Description of the Prior Art]In recent years, the expectation for small size and the nonaqueous electrolyte secondary battery which is lightweight and has high energy density is growing as portable-izing of apparatus and cordless making progress. The multiple oxide of lithium, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and LiMnO_2 , and a transition metal is known by the active material for nonaqueous electrolyte secondary batteries.

[0003]Research of the multiple oxide of lithium and manganese is briskly done in it as a cheap material whose safety is especially high these days. These are used for positive active material and development of the nonaqueous electrolyte secondary battery of the high tension by combining negative electrode active material, such as occlusion and a carbon material which can be emitted, and high energy density is furthered in lithium.

[0004]Generally, the positive active material used for a nonaqueous electrolyte secondary battery becomes lithium which is main active material from the multiple oxide which made transition metals including cobalt, nickel, and manganese dissolve. With kinds of the transition metal used, electrode characteristics, such as electric capacity, reversibility, operating potential, and safety, change.

[0005]For example, the nonaqueous electrolyte secondary battery which used for positive active material the R-3-m rhombohedron halite laminar multiple oxide which made cobalt and nickel dissolve like LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, While being able to attain 140 - 160 mAh/g and 180 - 200 mAh/g, and comparatively high capacity density, respectively, high voltage regions, such as 2.7-4.3V, show good reversibility.

[0006]

[Problem(s) to be Solved by the Invention]However, when a cell is warmed, since the problem on which a cell generates heat easily by the reaction of the positive active material at the time of charge and an electrolysis solution solvent, cobalt used as a raw material, and nickel are expensive, there is a problem to which the cost of an active material becomes high.

[0007]The proposal of $\text{LiNi}_{0.75}\text{Co}_{0.20}\text{Mn}_{0.05}\text{O}_2$ is made by JP,10-027611,A that the characteristic of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ should be improved. Although the proposal is made by JP,10-81521,A about the manufacturing method of the nickel manganese 2 element-system hydroxide raw material for lithium cells which has specific particle size distribution, In which thing, the positive active material with which it is simultaneously satisfied of three persons of charge-and-discharge capacity, cycle durability, and safety is not obtained.

[0008] LiMnO_2 of a prismatic crystal Pmm system or a monoclinic C2/m system, The cell using $\text{LiMn}_{0.95}\text{Cr}_{0.05}\text{O}_2$ or $\text{LiMn}_{0.9}\text{Al}_{0.1}\text{O}_2$, Although safety is high and there is an example which initial capacity reveals highly, change of the crystal structure accompanying a charging and discharging cycle takes place easily, and there is a problem which becomes insufficient [cycle durability].

[0009]. The proposal of $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ should do to each gazette of JP,5-283076,A, JP,8-171910,A, JP,2000-1240,A, and JP,2000-223157,A. Although the proposal of $\text{LiCo}_b\text{Mn}_c\text{M}_d\text{Ni}_{1-(b+c+d)}\text{O}_2$ is made by JP,11-25957,A, that with which all are satisfied of both capacity charge-and-discharge cycle durability and safety per capacity and volume per weight is not obtained.

[0010]It was made in order that this invention might solve such a technical problem, and the purpose has high capacity

and there is in providing the high safety positive electrode material for nonaqueous electrolyte secondary batteries excellent in charge-and-discharge cycle durability.

[0011]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is general formula $\text{Li}_{1-x}\text{Mn}_{1-x-y}\text{M}_y\text{O}_2$ (however, it is $0.30 \leq x < 0.65$ and $0 \leq y < 0.20$). Metallic element as which M is chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. It is expressed, A lithium containing transition metal multiple oxide for lithium secondary battery positive active material (henceforth "a multiple oxide of this invention"), wherein average valences of an element which consists of nickel, manganese, and the metallic element M are 2.700-2.970 is provided.

[0012] As a result of active oxygen's consisting is easy to be emitted of anodes when a cell is charged if the above-mentioned average valence is larger than 2.970, since it is easy to follow oxidation reaction of an electrolysis solution and the safety of a cell falls, it is not desirable.

[0013] Since it becomes impossible to be precisely filled up as a result of growth of an aggregated particle crystal growth is late and according to condensation of a crystal becoming slow at lithiation reaction time, if the above-mentioned average valence is larger than 2.970 when press molding of the active material is carried out, Since capacity per volume falls, or specific surface area of active material powder becomes high and the dissolution to an electrolysis solution of manganese takes place easily, it is not desirable.

[0014] In another side, if the above-mentioned average valence is smaller than 2.700, since capacity per weight will fall, it is not desirable. In this invention, especially desirable average valences are 2.850-2.950.

[0015] As for specific surface area of a multiple oxide of this invention, it is preferred that it is below $2\text{-m}^2/\text{g}$. If specific surface area exceeds $2\text{-m}^2/\text{g}$, since cell capacity falls temporally, in what is called a rocking chair [which it becomes easy to dissolve manganese in an anode in an electrolysis solution at the time of elevated-temperature use of a cell, and uses a carbon material especially for a negative electrode] type lithium ion battery, it is not desirable. Below $1\text{-m}^2/\text{g}$ of especially specific surface area is preferred.

[0016] As for a multiple oxide of this invention, it is preferred that it is an active material which has R-3-m rhombohedron structure from a field of charge-and-discharge cycle durability especially. In this invention, it is still preferred that a grating constant of an a-axis in R-3-m rhombohedron structure is 2.895-2.925Å, and a grating constant of c axis is 14.28-14.38Å. Since the safety of a cell, etc. will fall if a grating constant separates from this range, it is not desirable.

[0017] Exothermic starting temperature is not less than 255 **, and, as for this point, a multiple oxide of this invention is mentioned to one of the features of this invention. When exothermic starting temperature washes with a solvent an anode charged at 50 ** 4.3V by having made lithium into a counter electrode and carries out temperature up with ethylene carbonate, it means temperature by which a reaction with an electrolysis solution is started. [as used in this invention]

[0018] According to this invention, positive active material with high safety with exothermic starting temperature specially high as mentioned above is provided. Namely, exothermic starting temperature of the conventional LiCoO_2 at around 155 **. Exothermic starting temperature is around 175 ** as for a case of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. To exothermic starting temperature of LiMnO_4 being around 235 **, since a multiple oxide of this invention is as remarkable as not less than 255 ** and its exothermic starting temperature is high compared with them, the safety of a cell is improved.

[0019] According to this, it is preferred that it is more than 2.9 g/cm^3 , and granular material press density of a multiple oxide of this invention mixes a binder and a solvent to active material powder, makes them with a slurry, and coating and desiccation, and when it presses, it can make capacity per volume high at charge collector aluminum foil.

Especially desirable granular material press density is more than 3.1 g/cm^3 .

[0020] Granular material press density in this invention means apparent density gravity which calculated powder from volume and weight of a molding body when the hydraulic press was carried out by a pressure of 1 t/cm^2 . Positive active material by this invention The conventional manganese spinel LiMn_2O_4 , a lithium layer-like manganese compound, for example, granular material press density of LiMnO_2 , -- at most, since granular material press density is

high as several times compared with being about 2.6 g/cm^3 , It also has the feature which can make capacity density per volume of a cell remarkably higher than old lithium manganic acid ghost positive active material.

[0021] In the above-mentioned general formula $\text{LiNi}_x\text{Mn}_{1-x-y}\text{M}_y\text{O}_2$, since it becomes it difficult to take a stable R-3-m rhombohedron structure that x is less than 0.30, it is not desirable. If x exceeds 0.65, since safety will fall, it is not

desirable. Especially the desirable ranges of x are 0.40-0.55.

[0022] Since that it is one metallic element atom of Fe, Co, Cr, aluminum, Ti, Ga, In, and Sn can aim at improvement in charge-and-discharge cycle durability, safety, capacity, etc., the metallic element M is preferred. the addition of M is $0 < y \leq 0.20$ -- desirable -- 0.01 to 0.18 -- it is 0.05 - 0.16 especially preferably.

[0023] This invention is in charge of manufacturing the above-mentioned lithium containing transition metal multiple oxide for lithium secondary battery positive active material, A nickel manganese metallic element M coprecipitation conjugated compound and a lithium compound are mixed, and it is characterized by calcinating this mixture at 500 - 1000 ** in an inert atmosphere. As a lithium compound used for a reaction, lithium hydroxide, lithium carbonate, and lithium oxide are illustrated preferably.

[0024] As a nickel manganese metallic element M coprecipitation conjugated compound, A nickel manganese metallic element M salt water solution, an alkaline metal hydroxy compound, and an ammonium ion supply body are supplied to the system of reaction continuously or intermittently, respectively, A reaction is advanced, where it made temperature of the system of reaction into constant temperature within the limits of 30 - 70 ** and pH is held to constant value of 10 - 13 within the limits, General formula $\text{nickel}_x\text{Mn}_{1-x-y}\text{M}_y(\text{OH})_p$ (however, it is $0.30 < x \leq 0.65$,

$0 < y \leq 0.20$, and $2 < p \leq 4$.) M is chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. Nickel manganese metallic element M coprecipitation compound hydroxide which has the almost spherical particle shape acquired by making **** nickel manganese metallic element M coprecipitation compound hydroxide expressed, Or nickel manganese metallic element M coprecipitation compound oxy hydroxide produced by making an oxidizer act on the above-mentioned nickel manganese metallic element M coprecipitation compound hydroxide, Or it is preferred that it is especially either of the nickel manganese metallic element M coprecipitation multiple oxides produced by calcinating the above-mentioned nickel manganese metallic element M coprecipitation compound hydroxide or the above-mentioned nickel manganese metallic element M coprecipitation compound oxy hydroxide.

[0025]

[Embodiment of the Invention] The multiple oxide of this invention, for example Nickel manganese metallic element M coprecipitation compound hydroxide, The nickel manganese metallic element M coprecipitation compound powder chosen from nickel manganese metallic element M coprecipitation compound oxy hydroxide or a nickel manganese metallic element M coprecipitation multiple oxide, It is obtained by calcinating a mixture with lithium compound powder (preferably lithium hydroxide, lithium carbonate, lithium oxide) by 500 - 1000 ** of solid phase techniques under an inert gas atmosphere for 5 to 40 hours.

[0026] A temperature requirement is 750 - 950 ** especially preferably. If it calcinates in an oxygen containing atmosphere, for example, the atmosphere, since the average valence of the desired manganese nickel metal element M will become high, it is not desirable. As long as the average valences 2.70 - 2.97 of the manganese nickel metal element M specified to this invention are obtained, low-concentration oxygen may be contained in inactive gas. Although it depends for this allowable oxygen density also on calcination temperature and an active material presentation, 1000 ppm or less, 10 ppm or less, etc. are adopted suitably 1% or less, for example.

[0027] Positive electrode mixture is formed by mixing a carbon system conducting material and binding material, such as acetylene black, black lead, and Ketchen black, to the powder of the multiple oxide of this invention. Polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose, an acrylic resin, etc. are used for binding material. The slurry which consists of the solvent or carrier fluid of the powder of the multiple oxide of this invention, a conducting material, binding material, and binding material -- positive pole collectors, such as aluminum foil, -- coating -- it dries and rolls [press] and a positive active material layer is formed on a positive pole collector.

[0028] In the lithium cell using the multiple oxide of this invention as positive active material, carbonic ester is preferred as a solvent of an electrolytic solution. Carbonic ester can use both annular and a chain. Propylene carbonate, ethylene carbonate, etc. are illustrated as cyclic carbonate. As chain carbonic ester, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methylpropyl carbonate, methylisopropyl carbonate, etc. are illustrated.

[0029] It may be independent, or the above-mentioned carbonic ester may be used for two or more sorts, mixing. It may be used mixing with other solvents. If chain carbonic ester and cyclic carbonate are used together depending on the material of negative electrode active material, a discharge characteristic, cycle durability, and charge and discharge efficiency may be improvable. It is good also as a gel polymer electrolyte by adding a fluorination vinylidene-fluoropropylene copolymer (for example, Kiner by Atochem), and a fluorination vinylidene-perfluoro propylvinyl ether copolymer to these organic solvents, and adding the following solute.

[0030] As a solute, ClO_4^- , CF_3SO_3^- , It is preferred to use any one or more sorts of the lithium salt which uses BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- , $2(\text{CF}_3\text{SO}_2)\text{N}^-$, etc. as an anion. As for an above-mentioned electrolytic solution or

polymer electrolyte, it is preferred to add the electrolyte which consists of lithium salt by the concentration of 0.2 - 2.0 mol/L to the above-mentioned solvent or solvent content polymer. If it deviates from this range, ionic conductivity will fall and electrolytic electrical conductivity will fall. 0.5 - 1.5 mol/L is selected more preferably. Porous polyethylene and a porous polypropylene film are used for a separator.

[0031] The material which emits [occlusion and] a lithium ion is used for negative electrode active material. Although the material in particular that forms negative electrode active material is not limited, an oxide, carbon compounds, a silicon carbide compound, a silicon oxide compound, a titanium sulfide, a boron carbide compound, etc. which made the subject the metal of a lithium metal, a lithium alloy, a carbon material, the periodic table 14, and 15 fellows, for example are mentioned.

[0032] As a carbon material, what carried out the pyrolysis of the organic matter on various pyrolysis conditions, an artificial graphite, natural graphite, soil black lead, expanded graphite, scaly graphite, etc. can be used. The compound which makes the tin oxide a subject can be used as an oxide. Copper foil, nickel foil, etc. are used as a negative pole collector.

[0033] As for an anode and a negative electrode, it is preferred to knead an active material with an organic solvent, to consider it as a slurry, and to obtain this slurry by applying, drying and pressing it in it to a metal foil collector. There are no restrictions in particular in the shape of the lithium cell using the multiple oxide of this invention. A sheet shaped (what is called film state), the letter of folding, a wound type closed-end cylindrical shape, a button form, etc. are chosen according to a use.

[0034]

[Example] Next, although concrete Examples 1-9 and the comparative examples 1-3 of this invention are explained, this invention is not limited to these examples.

[0035] <<Example 1>> The metal sulfate-water solution, aqueous ammonia solution, and caustic soda aqueous solution containing nickel sulfate and manganese sulfate were continuously supplied so that pH in a reaction vessel might be set to 11.35. Temperature was held at 50 **. After the reaction, the slurry was rinsed [filtration] and dried, it was spherical and the nickel manganese coprecipitation hydroxide granular material with a mean particle diameter of 8 micrometers was obtained. This nickel manganese coprecipitation hydroxide granular material was calcinated and ground in the atmosphere at 550 **, and nickel manganese coprecipitation oxide powder was obtained. This nickel manganese coprecipitation oxide powder and lithium hydroxide powder were mixed, it calcinated and ground at 830 ** among a nitrogen gas atmosphere, and $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.902 Å and c axis of the grating constant of the a-axis was 14.32 Å. It was 2.917 when it asked for the average valence of nickel and manganese about this powder with the redox titration and the chelatometry which used FeSO_4 and KMnO_4 . The specific surface area of this powder was 0.78 m²/g. It was 3.15 g/cm³, when the hydraulic press of the obtained $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ powder was carried out by the pressure of 1 t/cm² and granular material press density was calculated from volume and weight. Ball mill mixing of this $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ powder, and acetylene black and polyvinylidene fluoride was carried out adding N-methyl pyrrolidone by the weight ratio of 83/10/7, and it was considered as the slurry. This slurry was applied on the 20-micrometer-thick aluminium foil positive pole collector, it dried at 150 **, and N-methyl pyrrolidone was removed. Roll press rolling was carried out to after an appropriate time, and the positive electrode body was obtained. Use 300-micrometer-thick metal lithium foil for a separator at a negative electrode using 25-micrometer-thick porous polyethylene, and nickel foil is used for a negative pole collector. To the electrolysis solution, the coin cell 2030 type was assembled within the argon glove box using 1M LiPF₆/EC+DEC (1:1). And constant current charge is carried out to 4.3V at 30 mA per 1g of positive active material under a 60 ** temperature atmosphere, Constant current discharge was carried out to 2.7V at 30 mA per 1g of positive active material, the charge-and-discharge cycle test was done 30 times, and the capacity maintenance rate was searched for from the ratio of the service capacity after 2 times charge and discharge, and the service capacity after 30 times charge and discharge. The short form sealing cell was assembled within the argon glove box using the same anode and separator, the negative electrode, and the electrolysis solution for primary safety evaluation. After charging this short form cell to 4.3V under a 50 ** temperature atmosphere, the cell was disassembled under the room temperature, and it asked for exothermic starting temperature when putting the anode into the well-closed container and carrying out temperature up to a sample using nothing and a differential-scanning-calorimetry device with ethylene carbonate. As for initial capacity, 149 mAh/g and the capacity maintenance rate were 283 ** in exothermic starting temperature 92%.

[0036]<<Example 2>> The metal sulfate-water solution containing nickel sulfate, manganese sulfate, and cobalt sulfate was used as a metal sulfate-water solution, and also the nickel manganese cobalt coprecipitation hydroxide granular material with a mean particle diameter of 8 micrometers was obtained like the above-mentioned Example 1. This nickel manganese cobalt coprecipitation hydroxide granular material was calcinated and ground in the atmosphere at 550 **, and also nickel manganese cobalt coprecipitation oxide powder was obtained. This nickel manganese cobalt coprecipitation oxide powder and lithium hydroxide powder were mixed, it calcinated and ground at 830 ** among a nitrogen gas atmosphere, and $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ with a mean particle diameter of 6 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.903 Å and c axis of the grating constant of the a-axis was 14.34Å. It was 2.873 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was $0.79\text{m}^2/\text{g}$. Granular material press density was 3.08 g/cm^3 . $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 155 mAh/g and the capacity maintenance rate were 275 ** in exothermic starting temperature 96%.

[0037]<<Example 3>> Used aluminum sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. A nickel manganese-aluminum coprecipitation oxide is compounded like the above-mentioned Example 2. Subsequently, lithium nickel manganese-aluminum multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Al}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.896 Å and c axis of the grating constant of the a-axis was 14.29Å. It was 2.923 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was $0.85\text{m}^2/\text{g}$. Granular material press density was 3.07 g/cm^3 . $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Al}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 150 mAh/g and the capacity maintenance rate were 286 ** in exothermic starting temperature 94%.

[0038]<<Example 4>> Used ferrous sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. The nickel ferromanganese coprecipitation oxide was compounded like the above-mentioned Example 2, and, subsequently lithium nickel ferromanganese multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Fe}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.901 Å and c axis of the grating constant of the a-axis was 14.33Å. It was 2.927 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was $0.83\text{m}^2/\text{g}$. Granular material press density was 3.05 g/cm^3 . $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Fe}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 151 mAh/g and the capacity maintenance rate were 280 ** in exothermic starting temperature 94%.

[0039]<<Example 5>> Used titanium sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. Nickel manganese-titanium coprecipitation hydroxide was compounded like the above-mentioned Example 2, and, subsequently lithium nickel manganese-titanium multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Ti}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.904 Å and c axis of the grating constant of the a-axis was 14.34Å. It was 2.918 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was $0.75\text{m}^2/\text{g}$. Granular material press density was 3.11 g/cm^3 . $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Ti}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 151 mAh/g and the capacity maintenance rate

were 285 ** in exothermic starting temperature 94%.

[0040]<<Example 6>> Used the chromium sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also, Nickel manganese chromium coprecipitation hydroxide was compounded like the above-mentioned Example 2, and, subsequently lithium nickel manganese chromium multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.902 Å and c axis of the grating constant of the a-axis was 14.32Å. It was 2.920 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.79m²/g. Granular material press density was 3.14 g/cm³. $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 153 mAh/g and the capacity maintenance rate were 288 ** in exothermic starting temperature 94%.

[0041]<<Example 7>> Used sulfuric acid gallium instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also, Nickel manganese gallium coprecipitation hydroxide was compounded like the above-mentioned Example 2, and, subsequently lithium manganese gallium multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Ga}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.899 Å and c axis of the grating constant of the a-axis was 14.30Å. It was 2.923 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.75m²/g. Granular material press density was 3.06 g/cm³. $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Ga}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 150 mAh/g and the capacity maintenance rate were 281 ** in exothermic starting temperature 93%.

[0042]<<Example 8>> Used indium sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also, The nickel manganese indium coprecipitation oxide was compounded like the above-mentioned Example 2, and, subsequently lithium manganese indium multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{In}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.922 Å and c axis of the grating constant of the a-axis was 14.36Å. It was 2.932 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.71m²/g. Granular material press density was 3.13 g/cm³. $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{In}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 155 mAh/g and the capacity maintenance rate were 282 ** in exothermic starting temperature 95%.

[0043]<<Example 9>> Used sulfuric acid tin instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also, The nickel manganese tin coprecipitation oxide was compounded like the above-mentioned Example 2, and, subsequently lithium manganese tin multiple oxide powder ($\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Sn}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.910 Å and c axis of the grating constant of the a-axis was 14.35Å. It was 2.900 when it asked for the average valence of nickel, manganese, and cobalt like Example 1 about this powder. The specific surface area of this powder was 0.85m²/g. Granular material press density was 3.10 g/cm³. $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Sn}_{0.10}\text{O}_2$ was used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 152 mAh/g and the capacity maintenance rate were 284 ** in exothermic starting temperature 94%.

[0044]<Comparative example 1> A nickel manganese coprecipitation oxide is compounded like the above-mentioned

Example 1, Subsequently, this nickel manganese coprecipitation oxide powder and lithium hydroxide powder were mixed, 8-hour calcination and grinding of were done at 830 °C among the atmosphere, and $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.888 Å and c axis of the grating constant of the a-axis was 14.32 Å. It was 2.997 when it asked for the average valence of nickel and manganese like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 9.62 m²/g. Granular material press density was 2.42 g/cm³. it was obtained by calcination among the atmosphere instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1 -- this -- it was $\text{LiNi}_{-0.50}\text{-Mn}_{-0.50}\text{-O}_2$ -used, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 149 mAh/g and the capacity maintenance rate were 238 % in exothermic starting temperature 92%.

[0045]<Comparative example 2> A nickel manganese cobalt coprecipitation oxide is compounded like the above-mentioned Example 2, Subsequently, this nickel manganese coprecipitation oxide powder and lithium hydroxide powder were mixed, 8-hour calcination and grinding of were done at 830 °C among the atmosphere, and $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.885 Å and c axis of the grating constant of the a-axis was 14.31 Å. It was 2.986 when it asked for the average valence of nickel and manganese like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 9.89 m²/g. Granular material press density was 2.41 g/cm³. This $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ obtained by calcination among the atmosphere instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1 was used, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 153 mAh/g and the capacity maintenance rate were 229 % in exothermic starting temperature 95%.

[0046]<Comparative example 3> Change nickel sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and the concentration of manganese sulfate, compound a nickel manganese cobalt coprecipitation oxide like the above-mentioned Example 2, and, subsequently like the above-mentioned comparative example 2 by calcination among the atmosphere. Lithium nickel manganese cobalt multiple oxide powder ($\text{LiNi}_{0.70}\text{Mn}_{0.20}\text{Co}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. It was 3.002 when it asked for the average valence of nickel and manganese like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 1.26 m²/g. It was $\text{LiNi}_{-0.70}\text{-Mn}_{-0.20}\text{-Co}_{-0.10}\text{-O}_2$ -used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 180 mAh/g and the capacity maintenance rate were 181 % in exothermic starting temperature 87%.

[0047]By reference, the result of the above-mentioned Examples 1-9 and the comparative examples 1-3 is summarized in the following table, and is shown.

[Table 1]

	α軸の格子定数 (Å)	c軸の格子定数 (Å)	平均粒径 (μm)	比表面積 (m ² /g)	密度プレス密度 (g/cm ³)	初期容量 (mAh/g)	容量維持率 (%)	昇熱温度 (°C)
実施例1	2.902	14.32	2.917	0.78	3.15	149	92	238
実施例2	2.903	14.34	2.878	0.79	3.08	155	96	275
実施例3	2.896	14.29	2.923	0.85	3.07	150	94	286
実施例4	2.901	14.33	2.927	0.89	3.05	151	94	290
実施例5	2.904	14.34	2.918	0.75	3.11	151	94	285
実施例6	2.902	14.32	2.920	0.78	3.14	153	94	288
実施例7	2.899	14.30	2.923	0.75	3.06	150	93	281
実施例8	2.922	14.36	2.932	0.71	3.13	155	95	282
実施例9	2.910	14.35	2.900	0.85	3.10	152	94	284
比較例1	2.888	14.32	2.997	9.62	2.42	149	92	238
比較例2	2.885	14.31	2.986	9.89	2.41	153	95	229
比較例3	—	—	3.002	1.26	—	180	87	181

[0048]

[Effect of the Invention] While an usable voltage range is wide and charge-and-discharge cycle durability is good by using the lithium content nickel manganese metallic element M multiple oxide of this invention as positive active material of a lithium secondary battery, the cell with high safety whose capacity is high is obtained.

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TECHNICAL FIELD

[Field of the Invention]This invention relates to the improved lithium containing transition metal multiple oxide which is used as positive active material of a lithium secondary battery.

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PRIOR ART

[Description of the Prior Art]In recent years, the expectation for small size and the nonaqueous electrolyte secondary battery which is lightweight and has high energy density is growing as portable-izing of apparatus and cordless making progress. The multiple oxide of lithium, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and LiMnO_2 , and a transition metal is known by the active material for nonaqueous electrolyte secondary batteries.

[0003]Research of the multiple oxide of lithium and manganese is briskly done in it as a cheap material whose safety is especially high these days. These are used for positive active material and development of the nonaqueous electrolyte secondary battery of the high tension by combining negative electrode active material, such as occlusion and a carbon material which can be emitted, and high energy density is furthered in lithium.

[0004]Generally, the positive active material used for a nonaqueous electrolyte secondary battery becomes lithium which is main active material from the multiple oxide which made transition metals including cobalt, nickel, and manganese dissolve. With kinds of the transition metal used, electrode characteristics, such as electric capacity, reversibility, operating potential, and safety, change.

[0005]For example, the nonaqueous electrolyte secondary battery which used for positive active material the R-3-m rhombohedron halite laminar multiple oxide which made cobalt and nickel dissolve like LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, being able to attain 140 - 160 mAh/g and 180 - 200 mAh/g, and comparatively high capacity density, respectively, high voltage regions, such as 2.7-4.3V, show good reversibility.

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EFFECT OF THE INVENTION

[Effect of the Invention] While an usable voltage range is wide and charge-and-discharge cycle durability is good by using the lithium content nickel manganese metallic element M multiple oxide of this invention as positive active material of a lithium secondary battery, the cell with high safety whose capacity is high is obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, when a cell is warmed, since the problem on which a cell generates heat easily by the reaction of the positive active material at the time of charge and an electrolysis solution solvent, cobalt used as a raw material, and nickel are expensive, there is a problem to which the cost of an active material becomes high.

[0007]The proposal of $\text{LiNi}_{0.75}\text{Co}_{0.20}\text{Mn}_{0.05}\text{O}_2$ is made by JP,10-027611,A that the characteristic of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ should be improved. Although the proposal is made by JP,10-81521,A about the manufacturing method of the nickel manganese 2 element-system hydroxide raw material for lithium cells which has specific particle size distribution, In which thing, the positive active material with which it is simultaneously satisfied of three persons of charge-and-discharge capacity, cycle durability, and safety is not obtained.

[0008] LiMnO_2 of a prismatic crystal Pmm system or a monoclinic C2/m system, The cell using $\text{LiMn}_{0.95}\text{Cr}_{0.05}\text{O}_2$ or $\text{LiMn}_{0.9}\text{Al}_{0.1}\text{O}_2$, Although safety is high and there is an example which initial capacity reveals highly, change of the crystal structure accompanying a charging and discharging cycle takes place easily, and there is a problem which becomes insufficient [cycle durability].

[0009]. The proposal of $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ should do to each gazette of JP,5-283076,A, JP,8-171910,A, JP,2000-294240,A, and JP,2000-223157,A. Although the proposal of $\text{LiCo}_b\text{Mn}_c\text{M}_d\text{Ni}_{1-(b+c+d)}\text{O}_2$ is made by JP,11-25957,A, that with which all are satisfied of both capacity charge-and-discharge cycle durability and safety per capacity and volume per weight is not obtained.

[0010]It was made in order that this invention might solve such a technical problem, and the purpose has high capacity and there is in providing the high safety positive electrode material for nonaqueous electrolyte secondary batteries excellent in charge-and-discharge cycle durability.

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is general formula $\text{LiNi}_x\text{Mn}_{1-x-y}\text{M}_y\text{O}_2$ (however, it is $0.30 \leq x \leq 0.65$ and $0 \leq y \leq 0.20$). Metallic element as which M is chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. It is expressed, A lithium containing transition metal multiple oxide for lithium secondary battery positive active material (henceforth "a multiple oxide of this invention"), wherein average valences of an element which consists of nickel, manganese, and the metallic element M are 2.700-2.970 is provided.

[0012] As a result of active oxygen's consisting is easy to be emitted of anodes when a cell is charged if the above-mentioned average valence is larger than 2.970, since it is easy to follow oxidation reaction of an electrolysis solution and the safety of a cell falls, it is not desirable.

[0013] Since it becomes impossible to be precisely filled up as a result of growth of an aggregated particle crystal growth is late and according to condensation of a crystal becoming slow at lithiation reaction time, if the above-mentioned average valence is larger than 2.970 when press molding of the active material is carried out, Since capacity per volume falls, or specific surface area of active material powder becomes high and the dissolution to an electrolysis solution of manganese takes place easily, it is not desirable.

[0014] In another side, if the above-mentioned average valence is smaller than 2.700, since capacity per weight will fall, not desirable. In this invention, especially desirable average valences are 2.850-2.950.

[0015] As for specific surface area of a multiple oxide of this invention, it is preferred that it is below $2\text{-m}^2/\text{g}$. If specific surface area exceeds $2\text{-m}^2/\text{g}$, since cell capacity falls temporally, in what is called a rocking chair [which it becomes easy to dissolve manganese in an anode in an electrolysis solution at the time of elevated-temperature use of a cell, and uses a carbon material especially for a negative electrode] type lithium ion battery, it is not desirable. Below $1\text{-m}^2/\text{g}$ of especially specific surface area is preferred.

[0016] As for a multiple oxide of this invention, it is preferred that it is an active material which has R-3-m rhombohedron structure from a field of charge-and-discharge cycle durability especially. In this invention, it is still more preferred that a grating constant of an a-axis in R-3-m rhombohedron structure is 2.895-2.925Å, and a grating constant of c axis is 14.28-14.38Å. Since the safety of a cell, etc. will fall if a grating constant separates from this range, it is not desirable.

[0017] Exothermic starting temperature is not less than 255 **, and, as for this point, a multiple oxide of this invention is mentioned to one of the features of this invention. When exothermic starting temperature washes with a solvent an anode charged at 50 ** 4.3V by having made lithium into a counter electrode and carries out temperature up with ethylene carbonate, it means temperature by which a reaction with an electrolysis solution is started. [as used in this invention]

[0018] According to this invention, positive active material with high safety with exothermic starting temperature specially high as mentioned above is provided. Namely, exothermic starting temperature of the conventional LiCoO_2 at around 155 **. Exothermic starting temperature is around 175 ** as for a case of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. To exothermic starting temperature of LiMn_2O_4 being around 235 **, since a multiple oxide of this invention is as remarkable as not less than 255 ** and its exothermic starting temperature is high compared with them, the safety of a cell is improved.

[0019] According to this, it is preferred that it is more than 2.9 g/cm^3 , and granular material press density of a multiple oxide of this invention mixes a binder and a solvent to active material powder, makes them with a slurry, and coating and desiccation, and when it presses, it can make capacity per volume high at charge collector aluminum foil.

Especially desirable granular material press density is more than 3.1 g/cm^3 .

[0020] Granular material press density in this invention means apparent density gravity which calculated powder from

volume and weight of a molding body when the hydraulic press was carried out by a pressure of 1 t/cm². Positive active material by this invention The conventional manganese spinel LiMn₂O₄, a lithium layer-like manganese compound, for example, granular material press density of LiMnO₂, -- at most, since granular material press density is as high as several steps compared with being about 2.6 g/cm³. It also has the feature which can make capacity density per volume of a cell remarkably higher than old lithium manganic acid ghost positive active material.

[0021] In the above-mentioned general formula LiNi_xMn_{1-x}MyO₂, since it becomes it difficult to take a stable R-3-m rhombohedron structure that x is less than 0.30, it is not desirable. If x exceeds 0.65, since safety will fall, it is not desirable. Especially the desirable ranges of x are 0.40-0.55.

[0022] Since that it is one metallic element atom of Fe, Co, Cr, aluminum, Ti, Ga, In, and Sn can aim at improvement in charge-and-discharge cycle durability, safety, capacity, etc., the metallic element M is preferred, the addition y of M atom is 0<y<0.20 -- desirable -- 0.01 to 0.18 -- it is 0.05-0.16 especially preferably.

[0023] This invention is in charge of manufacturing the above-mentioned lithium containing transition metal multiple oxide for lithium secondary battery positive active material, A nickel manganese metallic element M coprecipitation conjugated compound and a lithium compound are mixed, and it is characterized by calcinating this mixture at 500-1000 ** in an inert atmosphere. As a lithium compound used for a reaction, lithium hydroxide, lithium carbonate, and lithium oxide are illustrated preferably.

[0024] As a nickel manganese metallic element M coprecipitation conjugated compound, A nickel manganese metallic element M salt water solution, an alkaline metal hydroxy compound, and an ammonium ion supply body are supplied to the system of reaction continuously or intermittently, respectively, A reaction is advanced, where it made temperature of the system of reaction into constant temperature within the limits of 30-70 ** and pH is held to constant value of 10-13 within the limits, General formula nickel_xMn_{1-x}My(OH)_p (however, it is 0.30<x<0.65, 0<y<0.20, and 2<p<4.) M is chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. Nickel manganese metallic

element M coprecipitation compound hydroxide which has the almost spherical particle shape acquired by making **** nickel manganese metallic element M coprecipitation compound hydroxide expressed, Or nickel manganese metallic element M coprecipitation compound oxy hydroxide produced by making an oxidizer act on the above-mentioned nickel manganese metallic element M coprecipitation compound hydroxide, Or it is preferred that it is especially either of the nickel manganese metallic element M coprecipitation multiple oxides produced by calcinating the above-mentioned nickel manganese metallic element M coprecipitation compound hydroxide or the above-mentioned nickel manganese metallic element M coprecipitation compound oxy hydroxide.

[0025]

[Embodiment of the Invention] The multiple oxide of this invention, for example Nickel manganese metallic element M coprecipitation compound hydroxide, The nickel manganese metallic element M coprecipitation compound powder chosen from nickel manganese metallic element M coprecipitation compound oxy hydroxide or a nickel manganese metallic element M coprecipitation multiple oxide, It is obtained by calcinating a mixture with lithium compound powder (preferably lithium hydroxide, lithium carbonate, lithium oxide) by 500-1000 ** of solid phase techniques under an inert gas atmosphere for 5 to 40 hours.

[0026] A temperature requirement is 750-950 ** especially preferably. If it calcinates in an oxygen containing atmosphere, for example, the atmosphere, since the average valence of the desired manganese nickel metal element M will become high, it is not desirable. As long as the average valences 2.70-2.97 of the manganese nickel metal element M specified to this invention are obtained, low-concentration oxygen may be contained in inactive gas. Although it depends for this allowable oxygen density also on calcination temperature and an active material presentation, 1000 ppm or less, 10 ppm or less, etc. are adopted suitably 1% or less, for example.

[0027] Positive electrode mixture is formed by mixing a carbon system conducting material and binding material, such as acetylene black, black lead, and Ketchen black, to the powder of the multiple oxide of this invention. Polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose, an acrylic resin, etc. are used for binding material. the slurry which consists of the solvent or carrier fluid of the powder of the multiple oxide of this invention, a conducting material, binding material, and binding material -- positive pole collectors, such as aluminium foil, -- ring - it dries and rolls [press] and a positive active material layer is formed on a positive pole collector.

[0028] In the lithium cell using the multiple oxide of this invention as positive active material, carbonic ester is preferred as a solvent of an electrolytic solution. Carbonic ester can use both annular and a chain. Propylene carbonate, ethylene carbonate, etc. are illustrated as cyclic carbonate. As chain carbonic ester, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methylpropyl carbonate, methylisopropyl carbonate, etc. are illustrated.

[0029]It may be independent, or the above-mentioned carbonic ester may be used for two or more sorts, mixing. It may be used mixing with other solvents. If chain carbonic ester and cyclic carbonate are used together depending on the material of negative electrode active material, a discharge characteristic, cycle durability, and charge and discharge efficiency may be improvable. It is good also as a gel polymer electrolyte by adding a fluoridation vinylidene-hexafluoropropylene copolymer (for example, Kiner by Atochem), and a fluoridation vinylidene-perfluoro propylvinyl ether copolymer to these organic solvents, and adding the following solute.

[0030]As a solute, ClO_4^- , CF_3SO_3^- , It is preferred to use any one or more sorts of the lithium salt which uses BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- , $2(\text{CF}_3\text{SO}_2)\text{N}^-$, etc. as an anion. As for an above-mentioned electrolytic solution or polymer electrolyte, it is preferred to add the electrolyte which consists of lithium salt by the concentration of 0.2 - 2.0 mol/L to the above-mentioned solvent or solvent content polymer. If it deviates from this range, ionic conductivity will fall and electrolytic electrical conductivity will fall. 0.5 - 1.5 mol/L is selected more preferably. Porous polyethylene and a porous polypropylene film are used for a separator.

[0031]The material which emits [occlusion and] a lithium ion is used for negative electrode active material. Although the material in particular that forms negative electrode active material is not limited, an oxide, carbon compounds, a silicon carbide compound, a silicon oxide compound, a titanium sulfide, a boron carbide compound, etc. which made the subject the metal of a lithium metal, a lithium alloy, a carbon material, the periodic table 14, and 15 fellows, for example are mentioned.

[0032]As a carbon material, what carried out the pyrolysis of the organic matter on various pyrolysis conditions, an artificial graphite, natural graphite, soil black lead, expanded graphite, scaly graphite, etc. can be used. The compound which makes the tin oxide a subject can be used as an oxide. Copper foil, nickel foil, etc. are used as a negative pole collector.

[0033]As for an anode and a negative electrode, it is preferred to knead an active material with an organic solvent, to consider it as a slurry, and to obtain this slurry by applying, drying and pressing it in it to a metal foil collector. There are no restrictions in particular in the shape of the lithium cell using the multiple oxide of this invention. A sheet shaped (what is called film state), the letter of folding, a wound type closed-end cylindrical shape, a button form, etc. chosen according to a use.

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EXAMPLE

[Example]Next, although concrete Examples 1-9 and the comparative examples 1-3 of this invention are explained, this invention is not limited to these examples.

[0035]<<Example 1>> The metal sulfate-water solution, aqueous ammonia solution, and caustic soda aqueous solution containing nickel sulfate and manganese sulfate were continuously supplied so that pH in a reaction vessel might be set to 11.35. Temperature was held at 50 **. After the reaction, the slurry was rinsed [filtration] and dried, it was spherical and the nickel manganese coprecipitation hydroxide granular material with a mean particle diameter of 8 micrometers was obtained. This nickel manganese coprecipitation hydroxide granular material was calcinated and ground in the atmosphere at 550 **, and nickel manganese coprecipitation oxide powder was obtained. This nickel manganese coprecipitation oxide powder and lithium hydroxide powder were mixed, it calcinated and ground at 830 ** among a nitrogen gas atmosphere, and $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.902 Å and c axis of the grating constant of the a-axis was 14.32Å. It was 2.917 when it asked for the average valence of nickel and manganese about this powder with the redox titration and the chelatometry which used FeSO_4 and KMnO_4 . The specific surface area of powder was $0.78\text{m}^2/\text{g}$. It was 3.15 g/cm^3 , when the hydraulic press of the obtained $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ powder was carried out by the pressure of 1 t/cm^2 and granular material press density was calculated from volume and weight. Ball mill mixing of this $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ powder, and acetylene black and polyvinylidene fluoride was carried out adding N-methyl pyrrolidone by the weight ratio of 83/10/7, and it was considered as the slurry. This slurry was applied on the 20-micrometer-thick aluminium foil positive pole collector, it dried at 150 **, and N-methyl pyrrolidone was removed. Roll press rolling was carried out to after an appropriate time, and the positive electrode body was obtained. Use 300-micrometer-thick metal lithium foil for a separator at a negative electrode using 25-micrometer-thick porous polyethylene, and nickel foil is used for a negative pole collector. To the electrolysis solution, the coin cell 2030 type was assembled within the argon glove box using 1M LiPF₆/EC+DEC (1:1). And constant current charge is carried out to 4.3V at 30 mA per 1g of positive active material under a 60 ** temperature atmosphere, Constant current discharge was carried out to 2.7V at 30 mA per 1g of positive active material, the charge-and-discharge cycle test was done 30 times, and the capacity maintenance rate was searched for from the ratio of the service capacity after 2 times charge and discharge, and the service capacity after 30 times charge and discharge. The short form sealing cell was assembled within the argon glove box using the same anode and separator, the negative electrode, and the electrolysis solution for battery safety evaluation. After charging this short form cell to 4.3V under a 50 ** temperature atmosphere, the cell was disassembled under the room temperature, and it asked for exothermic starting temperature when putting the anode into the well-closed container and carrying out temperature up to a sample using nothing and a differential-scanning-calorimetry device with ethylene carbonate. As for initial capacity, 149 mAh/g and the capacity maintenance rate were 283 ** in exothermic starting temperature 92%.

[0036]<<Example 2>> The metal sulfate-water solution containing nickel sulfate, manganese sulfate, and cobalt sulfate was used as a metal sulfate-water solution, and also the nickel manganese cobalt coprecipitation hydroxide granular material with a mean particle diameter of 8 micrometers was obtained like the above-mentioned Example 1. This nickel manganese cobalt coprecipitation hydroxide granular material was calcinated and ground in the atmosphere at 550 **, and nickel manganese cobalt coprecipitation oxide powder was obtained. This nickel manganese cobalt coprecipitation oxide powder and lithium hydroxide powder were mixed, it calcinated and ground at 830 ** among a nitrogen gas atmosphere, and $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ with a mean particle diameter of 6 micrometers was compounded. X-ray

diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.903 Å and c axis of the grating constant of the a-axis was 14.34Å. It was 2.873 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.79m²/g. Granular material press density was 3.08 g/cm³. LiNi_{0.45}Mn_{0.45}Co_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 155 mAh/g and the capacity maintenance rate were 275 ** in exothermic starting temperature 96%.

[0037]<<Example 3>> Used aluminum sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. A nickel manganese-aluminum coprecipitation oxide is compounded like the above-mentioned Example 2, Subsequently, lithium nickel manganese-aluminum multiple oxide powder (LiNi_{0.45}Mn_{0.45}Al_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.896 Å and c axis of the grating constant of the a-axis was 14.29Å. It was 2.923 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.85m²/g. Granular material press density was 3.07 g/cm³. LiNi_{0.45}Mn_{0.45}Al_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 150 mAh/g and the capacity maintenance rate were 286 ** in exothermic starting temperature 94%.

[0038]<<Example 4>> Used ferrous sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. The nickel ferromanganese coprecipitation oxide was compounded like the above-mentioned Example 2, and, subsequently lithium nickel ferromanganese multiple oxide powder (LiNi_{0.45}Mn_{0.45}Fe_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.901 Å and c axis of the grating constant of the a-axis was 14.33Å. It was 2.927 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.83m²/g. Granular material press density was 3.05 g/cm³. LiNi_{0.45}Mn_{0.45}Fe_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 151 mAh/g and the capacity maintenance rate were 280 ** in exothermic starting temperature 94%.

[0039]<<Example 5>> Used titanium sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. Nickel manganese-titanium coprecipitation hydroxide was compounded like the above-mentioned Example 2, and, subsequently lithium nickel manganese-titanium multiple oxide powder (LiNi_{0.45}Mn_{0.45}Ti_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.904 Å and c axis of the grating constant of the a-axis was 14.34Å. It was 2.918 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.75m²/g. Granular material press density was 3.11 g/cm³. LiNi_{0.45}Mn_{0.45}Ti_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 151 mAh/g and the capacity maintenance rate were 285 ** in exothermic starting temperature 94%.

[0040]<<Example 6>> Used the chromium sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. Nickel manganese chromium coprecipitation hydroxide was compounded like the above-mentioned Example 2, and, subsequently lithium nickel manganese chromium multiple oxide powder (LiNi_{0.45}Mn_{0.45}Cr_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuK α of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.902 Å and c axis of the grating constant of

the a-axis was 14.32Å. It was 2.920 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.79m²/g. Granular material press density was 3.14 g/cm³. LiNi_{0.45}Mn_{0.45}Cr_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 153 mAh/g and the capacity maintenance rate were 288 ** in exothermic starting temperature 94%.

[0041]<<Example 7>> Used sulfuric acid gallium instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. Nickel manganese gallium coprecipitation hydroxide was compounded like the above-mentioned Example 2, and, subsequently lithium manganese gallium multiple oxide powder (LiNi_{0.45}Mn_{0.45}Ga_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.899 Å and c axis of the grating constant of the a-axis was 14.30Å. It was 2.923 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.75m²/g. Granular material press density was 3.06 g/cm³. LiNi_{0.45}Mn_{0.45}Ga_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 150 mAh/g and the capacity maintenance rate were 281 ** in exothermic starting temperature 93%.

[0042]<<Example 8>> Used indium sulfate instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. The nickel manganese indium coprecipitation oxide was compounded like the above-mentioned Example 2, and, subsequently lithium manganese indium multiple oxide powder (LiNi_{0.45}Mn_{0.45}In_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.922 Å and c axis of the grating constant of the a-axis was 14.36Å. It was 2.932 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 0.71m²/g. Granular material press density was 3.13 g/cm³. LiNi_{0.45}Mn_{0.45}In_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 155 mAh/g and the capacity maintenance rate were 282 ** in exothermic starting temperature 95%.

[0043]<<Example 9>> Used sulfuric acid tin instead of cobalt sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and also. The nickel manganese tin coprecipitation oxide was compounded like the above-mentioned Example 2, and, subsequently lithium manganese tin multiple oxide powder (LiNi_{0.45}Mn_{0.45}Sn_{0.10}O₂) with a mean particle diameter of 5 micrometers was compounded like the above-mentioned Example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.910 Å and c axis of the grating constant of the a-axis was 14.35Å. It was 2.900 when it asked for the average valence of nickel, manganese, and cobalt like Example 1 about this powder. The specific surface area of this powder was 0.85m²/g. Granular material press density was 3.10 g/cm³. LiNi_{0.45}Mn_{0.45}Sn_{0.10}O₂ was used instead of LiNi_{0.50}Mn_{0.50}O₂ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 152 mAh/g and the capacity maintenance rate were 284 ** in exothermic starting temperature 94%.

[0044]<Comparative example 1> A nickel manganese coprecipitation oxide is compounded like the above-mentioned Example 1. Subsequently, this nickel manganese coprecipitation oxide powder and lithium hydroxide powder were mixed, 8-hour calcination and grinding of were done at 830 ** among the atmosphere, and LiNi_{0.50}Mn_{0.50}O₂ with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.888 Å and c axis of the grating constant of the a-axis was 14.32Å. It was 2.997 when it asked for the average valence of nickel and manganese like the above-mentioned Example 1 about this powder. The specific surface area of this powder was 9.62m²/g. Granular material press density was 2.42 g/cm³. It was obtained by calcination

among the atmosphere instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1 -- this -- it was $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ - O_2 -used, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, the characteristic was evaluated. As for initial capacity, 149 mAh/g and the capacity maintenance rate were 238 ** in exothermic starting temperature 92%.

[0045]<Comparative example 2> A nickel manganese cobalt coprecipitation oxide is compounded like the above-mentioned Example 2, Subsequently, this nickel manganese coprecipitation oxide powder and lithium hydroxide powder were mixed, 8-hour calcination and grinding of were done at 830 ** among the atmosphere, and $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. By the Rietveld analysis, the grating constant of 2.885 Å and c axis of the grating constant of the a-axis was 14.31 Å. It was 2.986 when it asked for the average valence of nickel and manganese like the above-mentioned Example 1 about this powder. The specific surface area of this powder was $9.89\text{m}^2/\text{g}$. Granular material press density was 2.41 g/cm^3 . This $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.10}\text{O}_2$ obtained by calcination among the atmosphere instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1 was used, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 153 mAh/g and the capacity maintenance rate were 229 ** in exothermic starting temperature 95%.

[0046]<Comparative example 3> Change nickel sulfate in the metal sulfate-water solution of the above-mentioned Example 2, and the concentration of manganese sulfate, compound a nickel manganese cobalt coprecipitation oxide like the above-mentioned Example 2, and, subsequently like the above-mentioned comparative example 2 by calcination among the atmosphere. Lithium nickel manganese cobalt multiple oxide powder ($\text{LiNi}_{0.70}\text{Mn}_{0.20}\text{Co}_{0.10}\text{O}_2$) with a mean particle diameter of 5 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. It was 3.002 when it asked for the average valence of nickel and manganese like the above-mentioned Example 1 about this powder. The specific surface area of this powder was $1.26\text{m}^2/\text{g}$. It was $\text{LiNi}_{0.70}\text{Mn}_{0.20}\text{Co}_{0.10}\text{O}_2$ -used instead of $\text{LiNi}_{0.50}\text{Mn}_{0.50}\text{O}_2$ of the above-mentioned Example 1, and also the positive electrode body and the cell were produced like the above-mentioned Example 1, and the characteristic was evaluated. As for initial capacity, 180 mAh/g and the capacity maintenance rate were 181 ** in exothermic starting temperature 87%.

[0047]By reference, the result of the above-mentioned Examples 1-9 and the comparative examples 1-3 is summarized in the following table, and is shown.

Table 1)

	平均粒径 (Å)	平均粒径 (Å)	平均容量 (mAh/g)	比容量 (mAh/g)	密度 (g/cm ³)	初期容量 (mAh/g)	容量維持率 (%)	初期容量 (mAh/g)
実施例1	2.902	14.32	2.917	0.78	3.15	149	92	238
実施例2	2.903	14.34	2.873	0.79	3.03	155	95	275
実施例3	2.896	14.29	2.923	0.85	3.07	150	94	266
実施例4	2.901	14.33	2.927	0.83	3.05	151	94	280
実施例5	2.904	14.34	2.918	0.75	3.11	151	94	285
実施例6	2.902	14.32	2.920	0.79	3.14	153	94	288
実施例7	2.899	14.30	2.923	0.75	3.06	150	93	281
実施例8	2.922	14.36	2.932	0.71	3.13	155	95	292
実施例9	2.910	14.35	2.900	0.85	3.10	152	94	284
比較例1	2.886	14.32	2.997	0.82	2.42	149	92	238
比較例2	2.885	14.31	2.986	0.89	2.41	153	95	229
比較例3	—	—	3.002	1.29	—	180	87	181

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